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I, JULIE BILLINGSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2003900241 for a patent by BODO (BOB) HELLER as filed on 21 January 2003.

I further certify that the above application is now proceeding in the name of AUSTRALIAN ORGANIC RESOURCES PTY LTD pursuant to the provisions of Section 113 of the Patents Act 1990.

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WITNESS my hand this
Thirtieth day of January 2004

J. Billingsley

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# THE EXTRACTION AND TREATMENT OF HEAVY METALS IN SEWAGE SLUDGE
# THE HELLER PROCESS

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17th January 2003

## 1 Sewage sludges

Sewage sludges are anaerobically digested or aerated end products of waste-water treatment and purification. They represent about 10% of municipal waste production, are known for their non biodegradability and consequent persistence, and elevated organic pollutants (e.g. phenol, polychlorinated biphenyls, phthalates, etc.) and heavy metals and metalloids (As, Au, Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn)(Bloomfield and Pruden, 1975; Dean et al., 1972; Furr et al, 1976; Galloway, 1979; Hani, 1991; Jenkins et al., 1981; LeRiche, 1968; Lester, 1987a and 1987b; Mumma et al., 1983, 1984 and 1988; Reeves et al., 1999). Sludges accumulate as waste products in sewage treatment plants and are known to be good phosphate fertiliser (Bloomfield and Pruden, 1975). Eighty-two million tonnes (dried matter) accumulates globally every year.

The heavy metal content of sewage sludge is generally 0.1-2 wt.% on a dry weight basis (up to 4 wt.%). The heavy metals are derived from the paper and petrochemical industries, steelworks, foundries, chrome-plating, textiles, shampoos, cleaners, toothpaste, pipes, human excreta, etc. (Dean et al., 1972).

## 2. Environmental Considerations

Metals for which the world's governments set maximum acceptable levels in sludges to be used as fertiliser or as applied to the land include As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Se and Zn. Potential health hazards associated with the sludges are the uptake of these metals by aquatic life and plants and subsequent accumulation of the metals in the food chain (Tyagi and Couillard, 1987). The metals may also be leached from the soils and mobilised through ground water.

However for several reasons it is desirable that the sludges be treated to conform with Class A Bio-solid, principally;

- significantly enhanced $ value to the processor. Class A Bio-solids have much broader application than Class B.
- amelioration of the threat of toxic accumulation in soils.
- potential to reduce costs associated with incineration of sludges (research has shown that high levels of heavy metals are of detrimental affect to incineration). While the aim of AOR is not to incinerate sludges, the knowledge gained here may have value for similar processes.
- potential worldwide environmental/recycling significance.

## 3. The Heller Process

Considerable laboratory work has been conducted by Bob Heller and Australian Organic Resources (AOR) into the extraction of the heavy metals from sewage sludges. Numerous technical reports are available to support the conclusions contained in this summary.

**Features of this Provisional Patent application are as follows;**

Heavy metal laden sewage sludge is mixed with an inorganic or organic acid solution in a concentration of 0.2% to 10.0%, but at a preferred concentration of 1.0%. The preferred acid is sulphuric acid but may be phosphoric, nitric, citric, acetic, or any other acid. The ratio 1 part dried sludge to 2 parts acid solution is preferred but may be any ratio up to 1 part sludge (on a dry weight basis) to 10 parts acid solution.

Mild turbulence, either mechanical or by air sparging, is utilised to mix the sludge-acid for a period of 10 minutes to 12 hours. After this time, the liquid is allowed to settle then decanted from the mixture. Two components are now present; 1. A heavy metal laden acidic liquid and a solid product, depleted in heavy metals but with residual acidic liquor present. These two components are then treated as follows depending on the degree of heavy metal contamination initially;

**(A) For low contamination sludge** a simple separation of liquor is all that may be necessary. Allow the solids to settle and remove the clear liquor. Transfer the settled solids to a de-watering device such as a basket centrifuge, decanter, filter-press, Spirac or any other type of de-watering apparatus. Transfer the separated liquid phase to the bulk liquid.

1. To the heavy metal laden liquor is added sufficient pulverised limestone or sodium hydroxide or any other alkaline solution or material to bring the pH to above 7.0. At this point a precipitate forms which consists of an iron-aluminium-phosphate hydroxide in which the heavy metals are scavenged, rendering the remaining liquor heavy metal free or acceptably low. The precipitate is filtered by any suitable means but preferably using a centrifuge or filter-press. The liquor may be re-used in the process after adjustment of the acid level. Separated solids may in some cases be a valuable resource and recovered by smelting or by any other means.

2. It should be noted that by careful adjustment of the pH a partial separation of heavy metals from the iron-aluminium-phosphate can be effected. This will depend on the species and concentration of heavy metals present. In the circumstances where this is feasible the phosphate component can be returned to the product phase to reinforce the nutrient value of the final material. This is also part of the patent application.

3. The solid product from 1. above is blended with a quantity of pulverised limestone from 5.0% to 75.0% by weight of the mixture on a dry weight basis, to produce a product that is acceptable as either fertiliser or soil amendment material.

**(B) For higher contaminated sludges** an <u>Integrated Multiple Counter Flow</u> (IMCF) system forms part of this patent application. Due to the capacity of the sludge to retain the

aqueous phase even after de-watering (approximately 40% by weight) it becomes necessary to perform a second or third extraction. The efficiency of this stage is increased significantly if a Double Counter-flow (DCF), in particular or Triple Counter-flow (TCF) technique is employed.

For the DCF a processing equilibrium is established whereby fresh acid solution is used to treat heavy metal sludges that had been processed once with a previously used liquor. (ie. this is a circumstance where fresh acid is used to treat once depleted sludge). Subsequently the now twice extracted sludge is de-watered and treated with limestone or similar, as in (A) above. The "fresh acid" is now once used acid solution and as such is used to treat new incoming sludge. On completion of this step the de-watered sludge progresses to the final stage and the twice-used acid solution goes for processing with limestone as in (A) above. See fig.1.

The procedure may be extended to include three decontamination steps for each batch of sludge in a manner that extends the DCF to a TCF operation. The latter may in some cases be more efficient than the former but beyond a three-step process the operating complexities become too great to be of economic use for this application. However in more critical areas more processing steps may be of use.

Another feature of this process is that certain sequestering and complexing agents improve the extraction efficiency for heavy metals. It has been found that the following are particularly effective:

*Phosphonic acids generally, and in particular, Acetodiphosphonic acid, Aminotris (methylene phosphonic acid), (2-hydroxyethyl) iminobis-(methylene phosphonic acid), Ethylenediaminetetrakis-(methylene phosphonic acid), Hexamethylenediaminetetrakis-(methylenephosphonic acid), Diethylenetriaminepentakis-(methylene phosphonic acid) Ethylenediamine tetra acetic acid and it's salts*

It is a feature of this process that any of the above agents may be incorporated into the extraction process at any stage from 0.5% to 10% and particularly in a single step process and the final step of a DCF or TCF procedure.

In a further development this process has been adapted to treat fresh sewage sludge from anaerobic treatment plants. Sludge from the de-watering plant is placed in a fully enclosed pre-treatment vessel of suitable capacity and blended with recycled water equal to twice the sludge quantity. This material has a highly offensive odour due to in large part to the high hydrogen sulphide content. Two methods to treat and de-odours the sludge have been developed as follows:

1) The sludge blend is continuously stirred and oxygenated by any of the conventional means ie. mechanical, air purging etc. A proprietary bacterial nutrient blend is added to the mix in order to promote the growth of aerobic bacteria. Under these conditions sulphides in the sludge will be digested and oxidised to sulphur compounds. This normally take between twenty-four (24) and forty-eight (48) hours to complete and reduces the hydrogen sulphide level in the work place to a safe concentration. Sludge is then treated to remove heavy metals as above.

2) In the second method removal of the odour of hydrogen sulphide from the sludge is achieved as an integral part of the heavy metal removal process. Sludge is placed in a closed vessel and blended with re-cycled water as for the first method. However the head-space of the treatment vessel is modified and enlarged to accept the outlet of a suitable ozone generator and to receive controlled addition of sulphuric acid. The sludge blend is stirred or air purged to give good mixing and sulphuric acid added at a predetermined rate to release hydrogen sulphide from the sludge. Hydrogen sulphide escapes from the liquor and is oxidised by the ozone in the head-space to sulphuric acid which condenses and is returned to the sludge. Excess ozone must be allowed to decompose (half-life about 1/2 hour) in a delay chamber to very low levels prior to venting to atmosphere. This process results in an acidified sludge containing heavy metals already in solution and is the preferred method.

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